

PVC/Nematic 액정복합막의 전기광학특성

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Electro-optical Properties of PVC/Nematic Liquid Crystal Composite Films

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초 록 PVC/액정 복합막의 응집상태 및 전기광학 특성을 넓은 막조성(30~70wt% LC)에 걸쳐 조사하였다. 또한 optical contrast가 가장 좋은 40/60(PVC/LC) 중량조성으로 된 복합막에 대해서는 온도 및 외부교류전계의 주파수 및 진압응답을 측정할 결과 문턱 주파수는 20 V_{rms} 이하(1 kHz, 25 $^{\circ}C$), rise time 및 decay time은 모두 10ms 이하(100 V_{rms} , 1 kHz, 25 $^{\circ}C$)였다.

Abstract The state of aggregation and optical contrast of poly(vinyl chloride)(PVC)/nematic liquid crystal(LC) composite film have been studied for a wide range(30~70 wt% LC)of film composition. In addition, effects of temperature, frequency and voltage of the applied AC electric field on the film transmittance have been measured for a film containing 60 wt% LC, which showed maximum optical contrast. For this particular composition of film, the threshold voltage was smaller than 40 V_{rms} at 1 kHz, 25 $^{\circ}C$, and the rise time and decay time were smaller than 10ms at 100 V_{rms} , 1 kHz, and 25 $^{\circ}C$.

1. Introduction

Thin composite films composed of polymer and low molecular weight liquid crystal(LC) are potentially useful for a variety of electro-optic applications ranging from switchable window to active matrix projection display¹⁻⁵. In most common form, they consist of LC droplets dispersed in polymer matrix known as PDLC(polymer dispersed liquid crystal). NCAP(nematic curvilinear aligned phase) which is typically prepared by emulsification of LCs in aqueous polymer solution before the film is coated and allowed to dry is also used for a special type of PDLC. Depending mainly on the composition of the film, LCs also can form continuous phase in sponge polymer matrix.

In these films LCs are imbedded in polymer matrix, either as dispersed droplets or as continuous phase, and hence the films are self

supported in spite of the high fluidity of LCs⁶. This makes the films suitable for the fabrication of large area displays. The conventional LC devices have been limited to the small size ones due to the difficulty of fabrication in uniform thickness cell⁷. In the composite films matrix polymer is plasticized by the dissolved LC molecules, which significantly reduces the glass transition temperature(T_g) of polymer, and provides the film with high flexibility. In addition, the absence of polarizers substantially reduces light loss and increases the brightness of both direct view and project displays.

The operating principle of the composite film is fairly simple. In the absence of electric field (unpowered) LC molecules within each droplet or LC domain will adopt configuration which minimizes the free energy of the droplet under given boundary conditions, which are determined by polymer-LC interfacial interactions. Most often in PDLC the configuration of mini-

imum energy is a bipolar configuration where the axis for cylindrical symmetry is the axis for droplet^{8,9)}. The nematic LC molecule is optically uniaxial, and thus it has an ordinary refractive index(n_o) and extraordinary refractive index(n_e). Suppose a nematic director(n) makes an angle(θ) with the light propagation direction(k). Then light linearly polarized parallel to (n, k) plane sees a refractive index($n_{||}$) given by eq.(1).

$$n_{||} = \frac{n_o n_e}{(n_o^2 \cos^2 \theta + n_e^2 \sin^2 \theta)^{1/2}} \quad \dots(1)$$

For light linearly polarized perpendicular to the (n, k) plane, the refractive index(n_{\perp}) does not vary with θ , and is given by eq.(2).

$$n_{\perp} = n_o \quad \dots(2)$$

In the absence of external field, the orientation of optic axis and hence the nematic director varies randomly from droplet to droplet; consequently light propagating normal to the film surface will probe a range of refractive index between n_o and n_e ¹⁰⁻¹²⁾. These indices do not generally match with the refractive index of polymer(n_p), and light will be scattered by the droplet as far as the droplet has comparable size with the wave length of light. For the typical droplets(0.1~10 μ m), droplet concentration(~60 vol%), and the film thickness(~50 μ m), light scatters many times while passing through the film, and these multiple scatterings cause the translucence of the unpowered film³⁾.

When an electric field is applied across the film(powerd), the LC molecules will tend to align with their long axis parallel to the field. The extent of director orientation depends on the electric field. If, then n_o is close to n_e , there will be very little scattering and the film will be highly transparent^{11,12)}. For $n_o \geq n_e$, maximum transparence is obtained with normal in-

cidence due to the minium path length of the light. However, for $n_o < n_e$, maximum transmittance occurs at incident angle other than the normal where the space average refractive index(n_{ave}) of LC matches with n_p .

This paper considers the morphologies and electro-optic properties of composite films composed of poly(vinyl chloride)(PVC) and nematic type liquid crystal. Films(60 wt% LC) were prepared, the electro-optic performances of the films as a function of operating temperature, and voltage and frequency of the AC electric field were measured. Results were interpreted in terms of the aggregation state of the films and the solubility of LC in polymer.

EXPERIMENTAL

Materials

poly(vinyl chloride)(PVC)($n_o=1.5415$, $T_g=81^\circ\text{C}$) and a nematic mixture of phenyl cyclohexane and biphenyl cyclohexane derivatives (ZLI-3417-000, Merck)($n_e=1.6351$, $n_o=1.4979$, $T_{KN} < -30^\circ\text{C}$, $T_{NI}=94^\circ\text{C}$) were used as polymer matrix and LC.

Film Casting

Composite films were prepared by SIPS^{13,14)} (solvent induced phase separation) technique at room temperature. Approximately 2 wt% of PVC and LC at desired film compisition, was dissolved in chloroform. Homogenized solutions were cast on a glass plate, using an applicator to control the thickness. The thickness of the dried films were ~30 μ m.

Morphology

Morphologies of the composite films were studied using a scanning electron microscopy (SEM). LCs were first extracted in methanol at 25 $^\circ\text{C}$, and the films were dried overnight under vacuum. The weight loss upon extraction can be used to decide the continuity of LC domains in polymer matrix. When the LC domains are interconnected in three dimension, almost all of the LCs that was initially loaded

is extracted¹³⁾. The dried films were cryogenically (in liquid nitrogen) fractured, and sputter-coated with gold before viewing under SEM.

Electro-optic Measurements

For electro-optic measurements, the composite films were sandwiched between two indium/tin oxide (ITO) coated glass plates. When the effects of temperature were to be measured, the cell was placed in a heating stage to control temperature. The collimated beam of He/Ne laser (wave length of 632.8 nm) was passed through the film, normal to the film surface, and the transmitted light intensity without any polarizer was measured with a photodiode. The output from a function generator was amplified and used to drive the shutter. The drive signal and the response of the photodiode were monitored with a digital storage oscilloscope (Hitachi VC-6023). The distance between the cell and photodiode was about 300mm.

RESULTS AND DISCUSSION

Morphology

Figure 1 shows the typical SEM micrographs of the film cross sections, fractured at liquid nitrogen temperature. At lower LC loadings (30 wt%) LC forms spherical droplets imbedded in polymer matrix. Most of the droplets are submicrons in diameter. At higher LC loadings (60 wt%) LC forms larger droplets, order of several μm or up to about $10 \mu\text{m}$, and they form curved channel or continuous phase.

Transmittance vs. LC Content

Figure 2 shows the off-state, and on state (1 kHz, 200 V_{p-p}) transmittance of the film with varying content of LC (30~70 wt% LC). The off-state transmittance shows a drastic drop at the weight fraction of LC, $\omega=0.6$, and it is further decreased at $\omega=0.7$.

The off-state scattering in these films is mainly governed by the film morphology¹⁻²⁾. At



(a)



(b)

Fig. 1. SEM micrographs of cryogenically fractured PVC/LC films;

a) 70/30, and b) 40/60 by weight.

$\omega=0.3$ and 0.4 , most LC formed dispersed droplets. However only few of them are large enough to cause scattering and due to the insignificant number of scattering center, most lights transmits¹⁵⁾.

The film becomes optically heterogeneous at $\omega=0.6$ and 0.7 . However, the on-state transmittance at $\omega=0.7$ is insufficient to obtain significant optical contrast. Film for optical display should have high on-state transmittance as well as high off-state scattering. Therefore, film containing 60% LC is most desirable for optical display, and further measurements were done for this film.

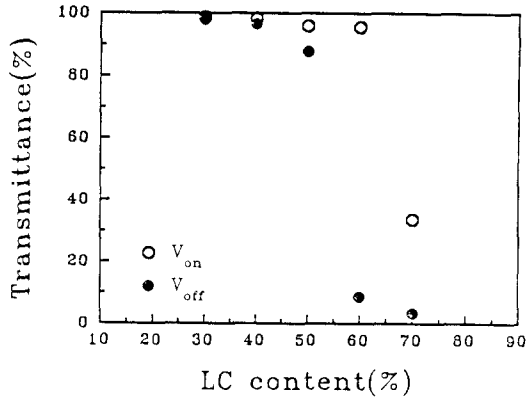


Fig. 2. Optical contrast of PVC/LC films vs. LC content
(power-on corresponds to 1 kHz, 200V_{p-p}, and 25°C)

Voltage Response

Transmittance, rise time(τ_r) and decay time (τ_d) of the films as a function of applied AC voltage are shown in Figures 3 and 4. Rise time is defined as the time for transmittance change from 10 to 90% upon turning the electric field-on, and the decay time as the time for the transmittance change from 90 to 10% upon turning the electric field-off. It should be mentioned that the transmittance response with voltage in Figure 3 corresponds to high frequency characteristics. In a high frequency range(Figure 5a), molecular orientation can not follow a superposed electric polarity change, and the transmittance output varies in a fashion of simple monotonic(not periodic) asymptote⁶. However, in a low frequency range(Figure 5b), a periodic flicker of transmitted light with twice of imposed frequency overlapping the asymptote was observed⁶. The electro-optic response of the composite films must be tailored for each application¹⁶. For switchable window and large area signs, films with high on-state clarity and off-state scattering is required, while driving voltage and switching speed are relatively unimportant. However, the high resolution active matrix applications require low driving voltage,

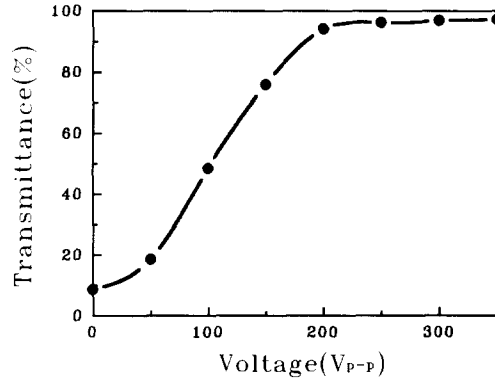


Fig. 3. Transmittance vs. applied voltage for PVC/LC(40/60) film at 1 kHz, 25°C

fast response time, and high resistivity.

The transmittance of powered film depends on average orientation of nematic directors, which is determined by the balance between electric and elastic torque¹. The elastic energy becomes large when the surface anchoring energy is large³. The surface anchoring energy basically depends on the polymer-LC interaction and director configuration. Consequently, the threshold voltage(V_{th}), defined as the voltage to raise the transmittance by 10%, depends on the director configuration. For comparable droplet size, bipolar configuration, which occurs in most cases, has substantially lower V_{th} than radial one, and it is given by eq. (3),

$$V_{th} = \frac{d}{3a} \left[\frac{\rho_p}{\rho_{LC}} + 2 \right] \left[\frac{K(1^2-1)}{\epsilon_0 \Delta\epsilon} \right]^{1/2} \dots\dots\dots(3)$$

where d, a, ρ , K, 1, ϵ_0 , and $\Delta\epsilon$ represent film thickness, major dimension, resistivity, elastic constant, aspect ratio(major dimension/minor dimension), dielectric constant in vacuum, and dielectric anisotropy, respectively. The subscript P and LC designate polymer and LC phase, respectively. Orientation of the bipolar configuration parallel to the long axis of the

cavity minimizes both the band and twist deformation energy. V_{th} is about $40 V_{p-p}$ (Figure 3) and the value is relatively high compared with typical PDLC film¹⁴⁾. This is probably due to the relatively strong interfacial interactions between PVC and LC, which on the other hand is caused by the polarity of PVC.

The rise time is given by eq.(4),¹⁾

$$\frac{1}{\tau_r} = \frac{1}{\eta} \frac{9\epsilon_0 \Delta \epsilon V^2}{d^2(\rho_p/\rho_{LC} + 2)^2} + \frac{K(1^2 - 1)}{\eta a^2} \dots (4)$$

where η is the viscosity, and other symbols bear the same meaning as defined earlier. In general τ_r is dominated by the first term, being inversely proportional to $\sim \Delta \epsilon V^2$ as shown qualitatively in Figure 4. It is seen that the τ_r is

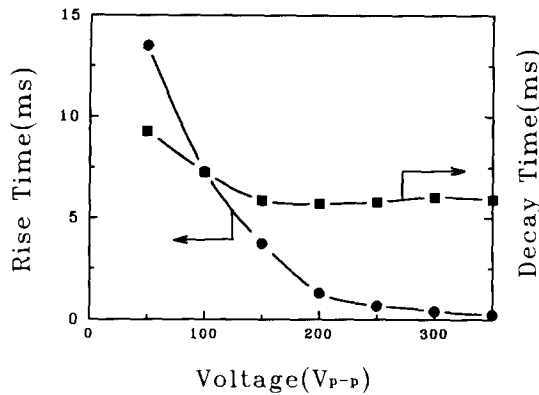


Fig. 4. Response times vs. applied voltage for PVC /LC(40/60) film at 1 kHz, 25°C

only a few ms or so, and this is faster than that of conventional twisted nematic type. The decay time is virtually independent on the applied voltage and is predicted by simply dropping the voltage term in eq. (4). τ_d is about 7 ms and is short while compared to other composite films as well as TN(twisted nematic) type¹⁾. This is due to the relatively strong PVC-LC interfacial interaction giving rise to high value of K.

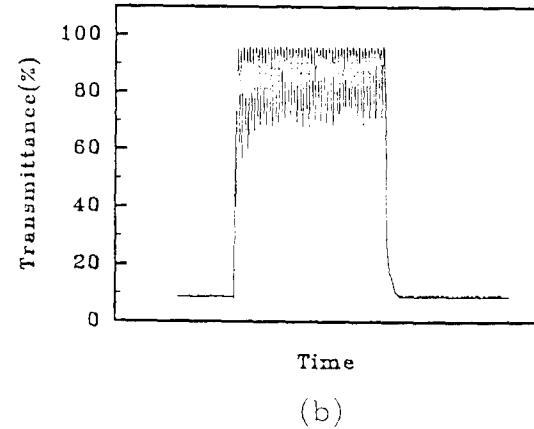
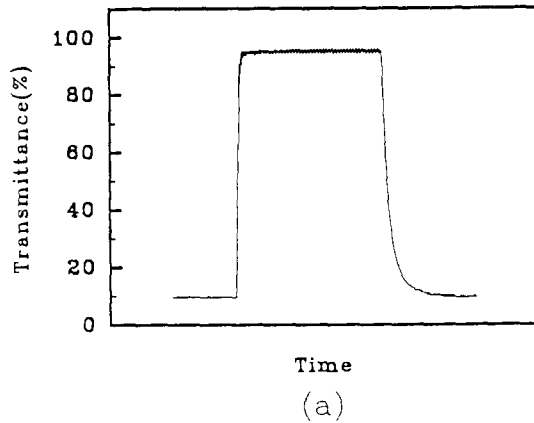


Fig. 5. Transmittance response a) at high (1 kHz) electric, and low(50 Hz) electric frequencies.

Frequency Response

Transmittance as a function of electric frequency is shown in Figure 6. The effect of frequency on electro-optic response comes into play via the partition of external electric field to LC phase(E_{LC}) and polymer phase(E_p) given by:²⁾

$$\frac{E_{LC}}{E_p} = \frac{|\epsilon_p^*|}{|\epsilon_{LC}^*|} = \left[\frac{\omega^2 \epsilon_p'^2 + \sigma_p'^2}{\omega^2 \epsilon_{LC}'^2 + \sigma_{LC}'^2} \right]^{1/2} \dots \dots \dots (5)$$

where E, ϵ^* , ϵ' , σ , and ω are amplitude of an A.C. electric field, complex dielectric constant,

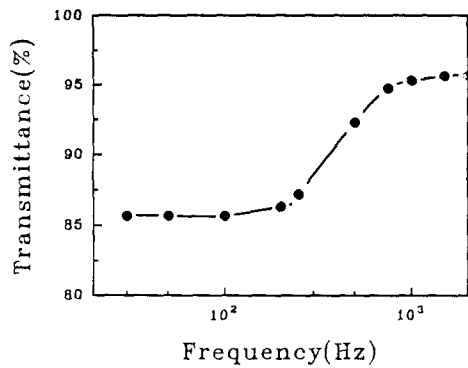


Fig. 6. Transmittance vs. electric frequency for PVC/LC(40/60) film at 200V_{r-r}, 25°C

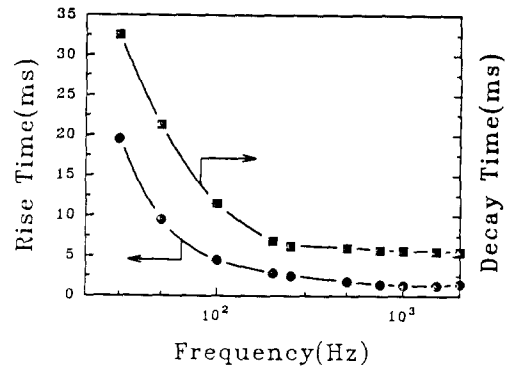


Fig. 7. Response times vs. electric frequency for PVC/LC(40/60) film at 200V_{r-r}, 25°C

dielectric constant, conductivity, and angular frequency, respectively.

At low enough and at high enough frequencies, this equation can be approximated as eq (6), and (7), respectively:

$$\frac{E_{i,c}}{E_p} \approx \frac{\sigma_p}{\sigma_{i,c}} \quad \text{conductivity region (low frequency)} \quad \dots\dots(6)$$

$$\frac{E_{i,c}}{E_p} \approx \frac{\epsilon_p'}{\epsilon_{i,c}'} \quad \text{dielectric region (high frequency)} \quad \dots\dots(7)$$

As the electric frequency decreases from dielectric to conductivity region, a transition occurs at frequencies corresponding to the relaxation of interfacial polarization, where $E_{i,c}/E_p$ drops abruptly. This occurs since the conductivity ratio ($\sigma_p/\sigma_{i,c}$) becomes much smaller than the dielectric ratio ($\epsilon_p'/\epsilon_{i,c}'$) because σ_p is much smaller than $\sigma_{i,c}$. This tendency is seen in Figure 6.

Rise time and decay time as a function of frequency are given in Figure 7. The response speed in these film is proportional to $\Delta\epsilon\epsilon_0 V^2$, as in eq. (4). Smaller partition of external field to LC phase at low frequency gives higher rise time⁶⁾, as our results indicate (Fig. 7). The effect of frequency on the decay time should come from the residual electric field in LC domain, and the degree of director orientation.

Effect of Temperature

The effect of temperature on the off-state transmittance of the film is shown in Figure 8. Transmittance increases slowly at lower and rapidly at higher temperature up to about 65 °C, beyond which the transmittance still increases with temperature never reaching a saturation.

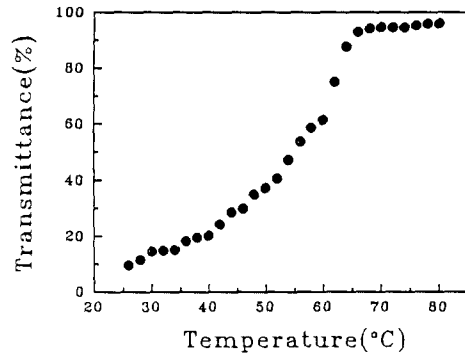


Fig. 8. Effect of temperature on the off-state transmittance of PVC/LC(40/60) film.

The increase of off-state transmittance with temperature is caused by the decrease in birefringence of LC¹⁷⁾, and increase of the solubility of LC in polymer phase. The extraordinary refractive index (n_e) decreases, and ordinary refractive index (n_o) increases with the increase of temperature, and the birefringence ($\Delta n = n_e - n_o$) decrease with temperature as^{18~20)},

$$\Delta n \propto \left[1 - \frac{0.98 T}{T_{NI}} \right]^{0.22} \dots\dots\dots(8)$$

where T is the absolute temperature, and T_{NI} is the nematic to isotropic transition temperature. As temperature increases, the solubility of LC in polymer increases. The refractive index of LC dissolved in polymer is its isotropic value(n_i) which is lower than n_e and higher than n_o . Therefore, mismatching of refractive index is significantly decreased with the increase of temperature giving rise to the increased transmittance. The clearing temperature(T_{NI}) of LC is also lowered due to the dissolution of polymer in LC. As the temperature increases, the solubility of LC in polymer is increased. SEM micrographs of quenched specimen showed that the smaller domains first disappeared, and the larger LC domains become smaller with the increase of temperature, and eventually the film becomes homogeneous at around 60°C. The source for scattering is disappeared.

CONCLUSION

The thin PVC films containing a nematic LC showed the highest optical contrast at 40/60 (PVC/LC by wt) composition, where LC domains were interconnected to form curved channels. For this film, the threshold voltage($\langle 40 V_{p-p}$), rise time and decay time($\langle 10$ ms at 100 V_{p-p}) were sufficiently low, and short for use in light valve.

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